Lyotropic Liquid-Crystalline Mesophases of $[Zn(H_2O)_6](NO_3)_2-C_{12}EO_{10}-CTAB-H_2O$ and $[Zn(H_2O)_6](NO_3)_2-C_{12}EO_{10}-SDS-H_2O$ Systems

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The mixture of two surfactants ($C_{12}EO_{10}$−CTAB and $C_{12}EO_{10}$−SDS) forms lyotropic liquid-crystalline (LLC) mesophases with $[Zn(H_2O)_6](NO_3)_2$ in the presence of a minimum concentration of 1.75 H_2O per $C_{12}EO_{10}$. The metal ion/$C_{12}EO_{10}$ mole ratio can be increased up to 8.0, which is a record high metal ion density in an LLC mesophase. The metal ion concentration can be increased in the medium by increasing the CTAB/$C_{12}EO_{10}$ or SDS/$C_{12}EO_{10}$ mole ratio at the expense of the stability of the LLC mesophase. The structure and some thermal properties of the new mesophase have been investigated using XRD, POM, FTIR, and Raman techniques.

Introduction

The lyotropic liquid-crystalline (LLC) properties of oligo(ethylene oxide) surfactants ($C_nH_{2n+1}(OCH_2CH_2)_mOH$, represented as C_nEO_m) with water[1] and water−oil mixtures[2] have been known in the literature for quite some time. Two or three surfactant systems, such as $H_2O-CTAB-C_nEO_m$, $H_2O-SDS-C_nEO_m$, and $H_2O-SDS-CTAB-C_nEO_m$ (CTAB is $C_{16}H_{33}N(CH_3)_3$-Br and SDS is $C_{12}H_{25}OSO_3Na$), have also been investigated in their micelle solution phases.[3] Many groups also presented the influence of salt ions on the $H_2O-C_nEO_m$ LLC mesophases[2c,4] and lyotropic metallomesogens.[4] However, the water−salt−surfactant (WSS) systems are stable only up to certain salt concentrations and depend on the counteranion of the salts.[5] Later, Dag et al. discovered the presence of a new LLC mesophase that contains a transition-metal salt and oligo(ethylene oxide), TMS−$C_{12}EO_{10}$, with a relatively high salt concentration.[6] In this self-assembly process, the coordinated water molecules, $M-OH_2$, can induce the self-assembly of the C_nEO_m molecules into LLC mesophases through hydrogen bonding ($M-OH_2-OCH_2CH_2$) and ion−dipole and ion−ion interactions.[6] Note also that the presence of the TMS−surfactant LLC phase has been investigated on TMS−pluronics and lanthanide−C_nEO_m systems.[7]

The importance of the TMS−surfactant mesophase is that it can be directly used to produce mesostructured metal oxides,[8] metal sulfides,[9] and metals,[10] which are not possible to synthesize using general mesostructured material synthesis methods. The mesostructured metal sulfides and metals have been synthesized using WSS LLC mesophases.[9,10] However, the WSS systems are not stable at the high metal ion density that it is necessary to produce stable extended mesostructured film materials. The other major problem in the WSS system is the evaporation of water from the media, which leads to the collapse of the mesophase before it is converted to mesostructured material. The TMS−C_nEO_m and TMS−pluronis LLC mesophases have many advantages: (i) the metal ion/surfactant mole ratio is quite high (the metal ion/EO unit is 0.32 in the $C_{12}EO_{10}$ and 0.25 in P123, $(HO(CH_2CH_2O)_{30}(CH(CH_3)CH_2O)_{70}(CH_2CH_2O)_{30}H)$[6,7] and (ii) no water evaporation problems in a salt−surfactant system (the TMS−surfactant LLC phase can also be used under vacuum conditions to produce mesostructured metal sulfide films).[11] However, the metal ion/surfactant mole ratio is still low compared to that of well-known mesostructured silica films (the Si/EO unit is 0.6−0.7).[5] Therefore, it is very important to investigate various salt−surfactant systems in this direction to increase the salt concentration further in the medium.

Results and Discussion

We have focused on two surfactant systems ($C_{12}EO_{10}$−CTAB and $C_{12}EO_{10}$−SDS) in the presence of $[Zn(H_2O)_6](NO_3)_2$ salt and water to investigate the LLC properties of the TMS−surfactants mesophases using FTIR, micro-Raman, POM with a temperature-controlled hot stage and XRD techniques. The $[Zn(H_2O)_6](NO_3)_2-C_{12}EO_{10}-CTAB$ and $[Zn(H_2O)_6](NO_3)_2-C_{12}EO_{10}-SDS$ samples were prepared in the absence and presence of extra water. The TMS/$C_{12}EO_{10}$ mole ratio has been varied between 1.0 (32.2% w/w salt/(salt + $C_{12}EO_{10}$) and 8.0 (79.2% w/w salt/(salt + $C_{12}EO_{10}$) in $[Zn(H_2O)_6](NO_3)_2-C_{12}EO_{10}-$

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(1) (a) Mitchell, D. J.; Tiddy, G. J. T.; Waring, L.; Bostock, T.; McDonald, M. P. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 975. (b) Sakya, P.; Seddon, J. M.; Templer, R. H.; Mirkin, R. J.; Tiddy, G. J. T. *Langmuir* **1997**, *13*, 3706. (c) Chernik, G. G. *Curr. Opin. Colloid Interface Sci.* **2000**, *4*, 381.

(2) (a) Iwanaga, T.; Suzuki, M.; Kunieda, H. *Langmuir* **1998**, *14*, 5775. (b) Kunieda, H.; Shigeta, K.; Ozawa, K.; Suzuki, M. *Langmuir* **1999**, *15*, 3118. (c) Kunieda, H.; Umizu, G.; Aramaki, K. *J. Phys. Chem. B* **2000**, *104*, 2005.

(3) (a) Gao, H. C.; Zhu, R. X.; Yang, X. Y.; Mao, S. Z.; Zhao, S.; Yu, J. Y.; Du, Y. R. *J. Colloid Interface Sci.* **2004**, *273*, 626. (b) Acharya, D. P.; Sato, T.; Kaneko, M.; Singh, Y.; Kunieda, H. *J. Phys. Chem. B* **2006**, *110*, 754.

(4) (a) Percec, V.; Tomazos, D.; Heck, J.; Blackwell, H.; Ungar, G. *J. Chem. Soc., Perkin Trans.* **1994**, *2*, 31. (b) Lee, M.; Cho, B.-K. *Chem. Mater.* **1998**, *10*, 1894. (c) Otake, T.; Ogasawara, M.; Ito-Akıta, K.; Nishina, N.; Ujiie, S.; Ohno, H.; Kato, T. *Chem. Mater.* **2000**, *12*, 782. (d) Donnio, B. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 371.

(5) Dag, Ö.; Verma, A.; Ozin, G. A.; Kresge, C. T. *J. Mater. Chem.* **1999**, *9*, 1475.

(6) Çelik, Ö.; Dag, Ö. *Angew. Chem., Int. Ed* **2001**, *40*, 3800.

(7) (a) Demirörs, A. F.; Eser, B. E.; Dag, Ö. *Langmuir* **2005**, *21*, 4156. (b) Albayrak, C.; Gülten, G.; Dag, Ö. *Langmuir* **2007**, *23*, 876. (c) Selivanova, N. M.; Lobkov, V. S.; Barabanov, V. P.; Salikhov, K. M.; Haase, W.; Galyametdinov, Y. G. *Dokl. Chem.* **2005**, *401*, 51.

(8) Attard, G. S.; Glyde, J. C.; Göltner, C. G. *Nature* **1995**, *378*, 366.

(9) Braun, P. V.; Osenar, P.; Stupp, S. I. *Nature* **1996**, *380*, 325.

(10) (a) Attard, G. S.; Barlett, P. N.; Coleman, N. R. B.; Elliott, J. M.; Owen, J. R.; Wang, J. H. *Science* **1997**, *278*, 838. (b) Yamauchi, Y.; Momma, T.; Yokoshima, T.; Kuroda, K.; Osaka, T. *J. Mater. Chem.* **2005**, *15*, 1987.

(11) Türker, Y.; Dag, Ö. *J. Mater. Chem.* **2008**, *18*, 3467.

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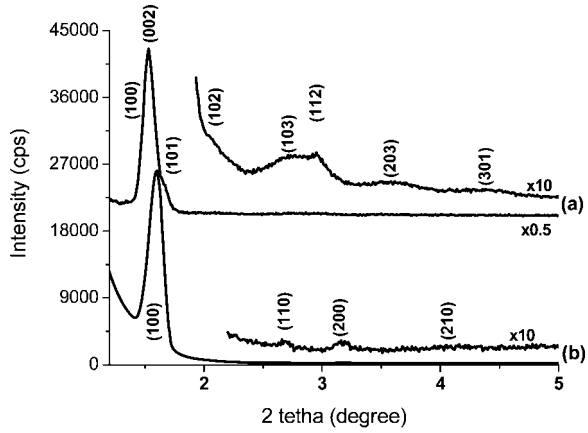

Figure 1. XRD patterns of the LLC mesophase of (a) fresh and (b) aged 6.0[$Zn(H_2O)_6$](NO_3)$_2$−$C_{12}EO_{10}$−0.5CTAB−7H_2O samples.

Figure 2. POM image of the LLC mesophase of 6.0[$Zn(H_2O)_6$]-(NO_3)$_2$−$C_{12}EO_{10}$−0.5CTAB−7H_2O.

CTAB and between 2.0 (48.7% w/w) and 8.0 (79.2% w/w) in [$Zn(H_2O)_6$](NO_3)$_2$−$C_{12}EO_{10}$−SDS. The charged surfactant/$C_{12}EO_{10}$ mole ratio has been changed between 0.0 and 1.0 (38.6% w/w CTAB/(CTAB + $C_{12}EO_{10}$)) for CTAB and 0.0 and 0.75 (25.6% w/w SDS/(SDS + $C_{12}EO_{10}$)) for SDS. The free-water content of the mixtures can be reduced to as low as 1.75 H_2O molecules per $C_{12}EO_{10}$ (4.8% w/w H_2O/(H_2O + $C_{12}EO_{10}$)) to keep the LLC mesophase stable. Notice that the H_2O/$C_{12}EO_{10}$ mole ratio is about 35 (50% w/w) in an ordinary H_2O−$C_{12}EO_{10}$ hexagonal LLC phase.[1] The evaporation of extra water leads to the slow crystallization of the salts from the LLC mesophase. However, the LLC phase can be recovered after crystallization if samples are kept in a humid environment. Note also that even 8[$Zn(H_2O)_6$](NO_3)$_2$−$C_{12}EO_{10}$−CTAB−H_2O is stable over several hours of water evaporation (Figure S1A). The LLC mesophase is stable in closed vials for several months or longer. It is a general trend in both CTAB and SDS systems that the solubility of TMS increases with increasing CTAB or SDS amount at the expense of the stability of the LLC mesophase.

Figure 1 displays XRD patterns of fresh and aged 6[$Zn(H_2O)_6$](NO_3)$_2$−$C_{12}EO_{10}$−0.5CTAB−7H_2O samples under ambient conditions. The diffraction pattern is characteristic of a 3D hexagonal LLC mesophase with a unit cell parameter a of 70.2 Å (Figure 1a). However, with the evaporation of excess water, a phase change is observed, resulting in a diffraction line shift to higher angles with a characteristic 2D hexagonal pattern. The diffraction pattern of the fresh sample has eight diffraction lines that can be indexed to the (100), (002), (101), (102), (103), (112), (203), and (301) planes of the 3D hexagonal mesophase. Note also that the plot of d-spacing values versus x (where $d = xa$ and $x = (8/10.667(h^2 + hk + k^2)+3l^2)^{1/2}$) is linear with an intercept of zero and a slope of 70.2 Å. However, the XRD pattern of the aged sample has four diffraction lines, corresponding to the (100), (110), (200), and (210) planes of the 2D hexagonal mesophase (Figure 1b). Note that the unit cell parameter a (a = 70.2 Å that shifts to 63.3 Å with water evaporation) of the new mesophase is much larger than that of the [$Zn(H_2O)_6$](NO_3)$_2$−$C_{12}EO_{10}$ LLC (a = 55.4 Å) and the mesostructured silica (a = 53.1 Å) obtained using $C_{12}EO_{10}$ and very much depends on the salt and water concentrations in the media. The [$Zn(H_2O)_6$](NO_3)$_2$−$C_{12}EO_{10}$−SDS−H_2O samples also have similar diffraction patterns at small angles (Figure S1B in Supporting Information).

The polarized optical microscopy (POM) image of an aged sample shows a fan texture characteristic of a 2D hexagonal mesophase (Figure 2). Note that the fan texture exists up to an 8.0 salt/$C_{12}EO_{10}$ mole ratio in both [$Zn(H_2O)_6$](NO_3)$_2$−$C_{12}EO_{10}$−CTAB−H_2O and [$Zn(H_2O)_6$](NO_3)$_2$−$C_{12}EO_{10}$−SDS−H_2O systems in a broad range of salt and CTAB concentrations. Interestingly, below 2.0 salt/$C_{12}EO_{10}$, the [$Zn(H_2O)_6$](NO_3)$_2$−$C_{12}EO_{10}$−SDS−H_2O mixture is insoluble. Note that the LLC mesophase of 2.0 salt/$C_{12}EO_{10}$ is stable in the presence of up to a mole ratio of 1/4 SDS/$C_{12}EO_{10}$ but is insoluble in the presence of ⩾3/8 SDS/$C_{12}EO_{10}$ mole ratios. To investigate the thermal properties of the new systems, we have recorded their isotropization temperatures (ITs) using a hot stage under the POM. The ITs of the new systems are in general low compared to that of the [$Zn(H_2O)_6$](NO_3)$_2$−$C_{12}EO_{10}$ LLC system[6] and decrease with increasing charged surfactants (CTAB or SDS) and salt concentrations. Note also that the LLC mesophase of $C_{12}EO_{10}$−CTAB without water is stable at low salt concentrations and has relatively higher IT values. (The thermal behavior of the new systems will be discussed elsewhere, but a small IT list is given in Table 1.) Both systems show similar responses to heating—a decreasing trend in IT with increasing salt, water, and charged surfactant concentrations; see Table 1.

Table 1. Isotropization temperatures (IT) of the [$Zn(H_2O)_6$](NO_3)$_2$−$C_{12}EO_{10}$−CTAB−H_2O and [$Zn(H_2O)_6$](NO_3)$_2$−$C_{12}EO_{10}$−SDS−H_2O LLC samples with various compositions[a]

composition [$Zn(H_2O)_6$](NO_3)$_2$−CTAB−H_2O				composition [$Zn(H_2O)_6$](NO_3)$_2$−SDS−H_2O			
M[b,c]	CTA[b]	H_2O[b]	IT(°C)	M[b,c]	SDS[b]	H_2O[b,d]	IT(°C)
3	0.5		81.0	3	0.125	3.5	80.2
3	0.5	3.5	67.6	3	0.25	3.5	71.5
3	0.5	35	53.7	3	0.375	3.5	54.5
4	0.5	3.5	67.7	3	0.5	3.5	I
4	0.5	14	61.5	4	0.125	3.5	71.8
4	0.5	28	54.2	4	0.375	3.5	64.1
6	0.5	3.5	59.5	4	0.5	3.5	I
6	0.5	7	53.7	4	0.5	3.5	59.4
6	0.5	21	44.0	6	0.5	1.8	56.1
6	0.75	3.5	58.0	6	0.5	7	49.2
6	1	3.5	57.0	6	0.5	21	L
6	1.5	3.5	50.0	6	0.25	3.5	L
6	0.5	14	55.8	6	0.375	3.5	57.6
6	0.75	14	59.7	6	0.75	3.5	46.1
6	1	14	57.0	7	0.5	3.5	48.0
8	1	10	47.0	8	0.75	3.5	32.4

[a] Number of moles of $C_{12}EO_{10}$ is 1.0 in all samples. [b] Mole ratios with respect to $C_{12}EO_{10}$. [c] M = [$Zn(H_2O)_6$](NO_3)$_2$. [d] I = insoluble and L = liquid.

Figure 3 displays a series of FTIR spectra of the LLC samples, obtained from the $C_{12}EO_{10}$−CTAB surfactant systems. The spectra were recorded either by spreading a thin layer of the LLC

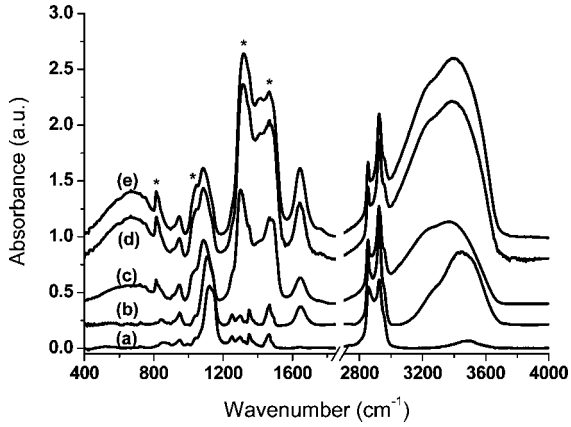

Figure 3. FTIR spectra of (a) $C_{12}EO_{10}$, (b) $C_{12}EO_{10}-0.5CTAB-H_2O$, (c) $3[Zn(H_2O)_6](NO_3)_2-C_{12}EO_{10}-0.5CTAB-H_2O$, (d) fresh $6[Zn(H_2O)_6](NO_3)_2-C_{12}EO_{10}-0.5CTAB-H_2O$, and (e) $6[Zn(H_2O)_6](NO_3)_2-C_{12}EO_{10}-0.5CTAB-H_2O$ aged for 1 day under ambient conditions (where * indicates the nitrate peaks).

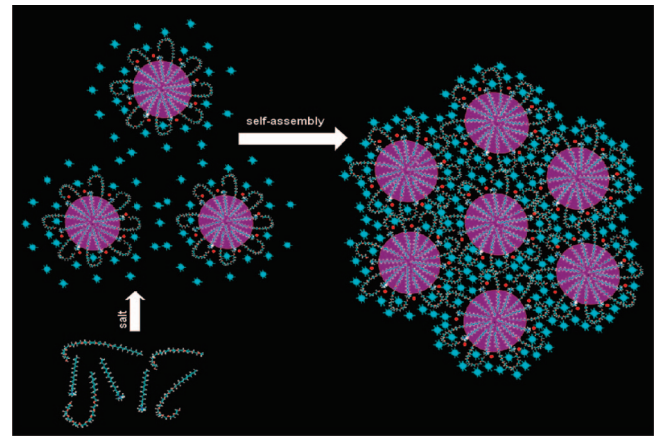

Figure 4. Schematic representation of the assembly of hexagonal mesophase. The core (purple regions) is alkyl tails of the charged and neutral surfactants, the ethylene oxides, and the charged head group of the charged surfactant, and metal ions (blue stars) are in the dark domains.

samples on a silicon surface or sandwiching the sample between two silicon wafers (which prevents the evaporation of water). Notice that the nitrate asymmetric stretching region (around 1290−1460 cm^{-1}) has the most intense peaks in the spectra because of the presence of an extensive number of nitrate ions incorporated into the LLC mesophases (details in Supporting Information, Figure S2A). The solvated CTAB molecules display characteristic peaks in the υ-CH regions (2600−2900 cm^{-1}); see Figure S2B. The shoulder at around 2850 cm^{-1} is also characteristic of a solvated CTAB species. Notice that the difference spectra between the $6.0[Zn(H_2O)_6](NO_3)_2-C_{12}EO_{10}-$**CTAB**$-7H_2O$ and $6.0[Zn(H_2O)_6](NO_3)_2-C_{12}EO_{10}-$**0.5 CTAB**$-7H_2O$ samples, where the only change is in the CTAB concentration, clearly show that the CTAB ions are not solvated in the crystalline form in the LLC media. The υ-CO mode of ethylene oxide units of $C_{12}EO_{10}$ is also very sensitive to its environment. The υ-CO mode, which is observed at 1120 cm^{-1} in pure $C_{12}EO_{10}$, shifts to 1110 cm^{-1} in the presence of water, to 1094 cm^{-1} in the presence of water and salt ions, and to 1080 cm^{-1} in the presence of only salt ions. The trend indicates that the strongest interaction is between coordinated water species and ethylene oxide units. The FTIR and Raman spectra of a series of $[Zn(H_2O)_6](NO_3)_2-C_{12}EO_{10}-$SDS-$H_2O$ samples were also recorded over a broad range of salt and SDS concentrations. The difference spectra, between the spectra of $5[Zn(H_2O)_6](NO_3)_2-C_{12}EO_{10}-0.5SDS-7H_2O$ recorded right after spreading the sample on a silicon wafer and 5, 10, and 15 min after spreading, show changes in the nitrate, sulfate, and ethylene oxide regions (Figure S2C). The most intense peaks of the sulfate headgroup, υ-SO_3 asymmetric modes at 1220 and 1253 cm^{-1}, shift to 1178 and 1256 cm^{-1} in the LLC mesophase, respectively, indicating that the sulfate headgroup of SDS strongly interacts with the positively charged metal species (Figure S2D). Also note that the peak at 954 cm^{-1} is assigned to the gauge conformer[13] of the ethylene oxide unit that appears in the difference spectra. It indicates that some trans-EO goes to gauge-EO upon water evaporation. The conformational change reduces the thickness of the ethylene oxide hydrophilic shells. This is consistent with the shift of the diffraction lines to higher angles upon water evaporation and it is the likely reason for the phase change from the 3D to 2D hexagonal structure.

Notice that the metal ion concentrations in the new systems, $[Zn(H_2O)_6](NO_3)_2-C_{12}EO_{10}-$CTAB and $[Zn(H_2O)_6](NO_3)_2-C_{12}EO_{10}-$SDS are 2 to 3 times higher compared to that of $[Zn(H_2O)_6](NO_3)_2-C_{12}EO_{10}$ and are comparable to the $SiO_2/C_{12}EO_{10}$ mole ratio (about 6 to 7) in the mesostructured silica.[5] The surfactant molecules mix well in the LLC mesophase to form a charged interface in the hydrophobic alkyl tail and ethylene oxide interface region. The interaction between the charged surfactant and oligo(ethylene oxide) enhances the hydrophobicity of the core (by alkyl tails and hydrophobic force) and the hydrophilicity of the EO shell (by the charged head groups); see schema in Figure 4. The charged surfactants create a positive (CTAB) or negative (SDS) charge at the hydrophobic (alkyl tail)−hydrophilic (ethylene oxide units) interface. In the case of the cationic surfactant, there is an $NS^+A^-M^+$ interaction (where NS^+ is a micelle of $C_{12}EO_{10}-CTA^+$ complex cation, A^- is the counteranion, and M^+ is $[Zn(H_2O)_6]^{2+}$ or $[Zn(H_2O)_x(O_2NO)]^+$ ions), and in the case of the anionic surfactant, there is an $NS^-M^+A^-$ interaction (where NS^- is a micelle of $C_{12}EO_{10}-DS^-$ complex anion), which allows the system to dissolve more TMS at this interface. Both the hydrogen bonding and electrostatic interactions between the charged surfactants and salt ions in the system make the salt−surfactant LLC mesophase stable at very high salt concentrations.

Conclusions

In summary, the surfactant molecules interact with each other in both the hydrophobic core and hydrophilic shell of the assembly to maintain much larger numbers of salt ions in their LLC mesophases. The stable samples require a small number of water molecules in the media. Note that the salt$-C_{12}EO_{10}$ system becomes liquid in the presence of extra water. However, in the two surfactants systems the free water is necessary to prevent the crystallization of salt ions. The evaporation of water from the media causes a 3D to 2D hexagonal phase change and promotes the crystallization of salt ions. Further studies are required to elucidate the structures and phase behaviors of the new salt−two surfactant LLC mesophases. The LLC mesophases of the other first-row and some second-row TMSs in the TMS$-C_nEO_m-$CTAB (or SDS)$-H_2O$ and TMS−pluronic−CTAB (or SDS)$-H_2O$ systems need to be investigated. The new

(12) Dag, Ö.; Samarskaya, O.; Tura, C.; Günay, A.; Çelik, Ö. *Langmuir* **2003**, *19*, 3671.

(13) Kimura, N.; Umemura, J.; Hayashi, S. *J. Colloid Interface Sci.* **1996**, *182*, 356.

mesophases with such high metal ion density can be used to produce mesostructured materials that are not possible with current synthesis methods.

Experimental Section

The new TMS−$C_{12}EO_{10}$−CTAB−H_2O LLC system is prepared by dissolving 0.475−3.800 g of $[Zn(H_2O)_6](NO_3)_2$ salt (corresponding to a 1–8 salt/$C_{12}EO_{10}$ mole ratio) in 0.050−0.800 g of water (corresponding to a 1.75–28 $H_2O/C_{12}EO_{10}$ mole ratio), 1.000 g of $C_{12}EO_{10}$, and 0.0−0.581 g of CTAB (corresponding to a 0.0−1.00 CTAB/$C_{12}EO_{10}$ mole ratio) by continuous shaking in closed vials at 50 °C for 1 day and then at 70 °C for another day. For example, the $6[Zn(H_2O)_6](NO_3)_2$−$C_{12}EO_{10}$−0.5CTAB−$7H_2O$ sample contains 2.850 g of $[Zn(H_2O)_6](NO_3)_2$, 1.000 g of $C_{12}EO_{10}$, 0.290 g of CTAB, and 0.200 g of H_2O. Similarly, the $[Zn(H_2O)_6](NO_3)_2$−$C_{12}EO_{10}$−SDS−H_2O samples were prepared using the same procedure and SDS instead of CTAB. In those, the samples contained 0.950−3.800 g of the $[Zn(H_2O)_6](NO_3)_2$ salt, 1.000 g of $C_{12}EO_{10}$, 0.0−0.460 g of SDS, and 0.05−0.800 g of H_2O.

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Supporting Information Available: XRD patterns for the 8/1 salt/$C_{12}EO_{10}$ mole ratio of TMS−$C_{12}EO_{10}$−CTAB−H_2O and TMS−$C_{12}EO_{10}$−SDS−H_2O systems, several FTIR and Raman spectra of the TMS−$C_{12}EO_{10}$−CTAB and TMS−$C_{12}EO_{10}$−SDS systems, and instrumentation. This material is available free of charge via the Internet at http://pubs.acs.org.

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